云南植物研究 1991; 13(2): 231—232
Acta Botanica Yunnanica
ISSN 0253-2700
CN 53-1039

裂冠牛奶菜中一新奇C_{21}甾体甙*

A NOVEL C_{21} STEROIDAL GLYCOSIDE FROM MARSDENIA INCISA*

CHEN Ji-Jun, ZHANG Zhuang-Xin, ZHOU Jun**
WANG De-Zu, ZHOU Lin, TAO Guo-Da

(*Laboratory of Phytochemistry, Kunming Institute of Botany, Academia Sinica*, Kunming 650204)

Key words Novel C_{21} steroidal glycoside; *Marsdenia incisa*; Asclepiadaceae

Besides a series of normal C_{21} steroids from *Marsdenia incisa* incisa P.T.Li et Y.P.Li, a small amount of novel C_{21} steroidal glycoside (Ⅰ) had been isolated. The mild acidic hydrolysis of (Ⅰ) afforded genin-(Ⅰ). By spectroscopic analyses of IR, EIMS, FDMS, ^{1}H NMR, ^{13}C NMR (DEPT, PRFT), ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY for (Ⅰ) and (Ⅱ), (Ⅰ) had been deduced as B-nor (7) -6β-formyl-pregnane-3β, 5β, 8β, 12β, 14β, 17β, 20-heptatol, named neomarinogenin; (Ⅱ) had been deduced as neomarinogenin 3-O-β-D-thevetopyranosyl- (1→4) -β-D-cymaropyranosyl- (1→4) -β-D-cymaropyranoside, named neomarinoside. Their physical and spectral data were as follows.

Neomarinogenin (Ⅰ). A colorless prism from Me_2CO, mp 202—205°C, $[\alpha]_D^{17}$ + 28.81° (MeOH, c 0.05), $C_{21}H_{34}O_8$ (Found: C, 60.76; H, 8.19, $C_{21}H_{34}O_8$ requires C, 60.87. H, 8.21%); IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1700 (C=O), 1050 (C-O-C); EIMS m/z: 397 (M-OH), 380 (397-OH), 379, 378 (M-2H_2O), 36; (M-3H_2O), 342 (M-4H_2O), 333, 315, 287, 43 (base peak). ^{1}H NMR (400 MHz, pyridine-d_5): 1.38 (3H, s, 19-Me), 1.60 (3H, d, J = 6.4Hz, 21-Me), 2.06 (3H, s, 18-Me), 2.58 (1H, d, J = 4.4Hz, 7-H), 4.08 (1H, m, 3-Ha), 4.48 (1H, q, J = 5.6Hz, 20-H), 4.62 (1H, dd, J = 9.6, 6.8 Hz, 12-Ha), 10.59 (1H, d, J = 4.4 Hz, 6-H); ^{13}C NMR (100.614 MHz, pyridine-d_5); 34.52 (t, C-1), 29.39 (t, C-2), 64.77 (d, C-3), 40.92 (t, C-4), 85.97 (s, C-5), 205.27 (d, C-6), 64.17 (d, C-7), 85.34 (s, C-8), 47.75 (d,

* This work was supported by grants from International Foundation for Science in Sweden and National Science Foundation of China.

** Author to whom correspondence should be addressed.

C-9), 45.79 (s, C-10), 27.96 (t, C-11), 72.68 (d, C-12), 60.02 (s, C-13), 88.92 (s, C-14), 34.52 (t, C-15), 33.35 (t, C-16), 87.43(s,C-17), 12.17 (q, C-18), 19.58 (q, C-19), 72.68 (d, C-20), 17.88 (q, C-21)。

Neomarinoside (Ⅱ), A white powder from MeOH, mp 150—155°C, $[\alpha]_D^{15}$ -2.37° (MeOH, c 0.10), $C_{42}H_{70}O_{18}$ (Found: C, 53.78; H, 8.31; $C_{42}H_{70}O_8 \cdot 4H_2O$ requires: C, 53.96; H, 8.35%), IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1700(C=O), 1050—1100 (C-O-C), FDMS m/z: 885 $(M+Na)^+$; ^1H NMR (500MHz, pyridine-d_5): 1.28 (3H, s, 19-Me), 1.36 (3H, d, J=6.2 Hz, 6'''-Me), 1.49 (3H, d, J=6.1 Hz, 21-Me), 1.58 (3H, d, J=6.0 Hz, 6''-Me), 1.59 (3H, d, J=6.2 Hz 6'-Me), 2.46 (1H, d, J=4.3 Hz, 7-H), 3.45 (1H, dd, J=9.6, 2.8 Hz, 4'-H), 3.55 (3H, s, 3'-OMe), 3.56 (3H, s, 3''-OMe), 3.58 (1H, dd, J=10.7, 3.3 Hz, 4''-H), 3.61 (1H, dd, J=9.9, 6.0 Hz, 4'''-H), 3.62 (1H, dd, J=8.5, 6.0, Hz, 3'''-H), 3.73 (1H, dq, J=9.3, 6.2 Hz, 5'''-H), 3.90 (3H, s, 3'''-OMe), 3.93 (1H, m, 3-H), 3.96 (1H, dd, J=9.0, 6.5 Hz, 2'''-H), 4.03 (1H, dd, J=12.8, 3.3 Hz, 12-H_a), 4.05 (2H, ddd, J=3.6, 3.0, 2.7 Hz, 3' and 3''-H), 4.16 (1H, dq, J=9.4, 6.1 Hz,5''-H), 4.20 (1H, dq, J=9.3, 6.0 Hz, 4'-H), 4.45 (1H, q, J=6.4 Hz,20-H), 4.76 (1H, d, J=7.8 Hz, 1'''-H), 5.09 (1H, dd, J=9.6, 1.8Hz, 1''-H), 5.24 (1H,dd, J=9.5, 1.8 Hz, 1'-H), 10.50 (1H, d, J=4.3 Hz, 6-H; ^{13}C NMR (125.759 MHz, pyridine-d_5): 34.48 (t, C-1), 26.91 (t, C-2), 72.76(d, C-3), 37.36 (t, C-4), 85.42 (s, C-5), 205.28 (d, C-6), 85.40 (s, C-8), 46.71 (d, C-9), 45.67 (s, C-10), 27.87 (t, C-11),72.66(d, C-12), 60.06 (s, C-13), 89.02 (s, C-14), 33.82 (t, C-15), 33.54(t, C-16),87.37(s, C-17), 12.30 (q, C-18), 19.80 (q, C-19), 72.60 (d, C-20), 17.87(q, C-21), 97.81 (d, C-1'), 36.87 (t, C-2'), 77.89 (d, C-3'), 83.08(d, C-4'), 69.04 (d, C-5'), 18.55 (q, C-6'), 58.74 (q, C-7'), 100.37 (d, C-1''), 37.09 (t, C-2''), 78.13 (d, C-3''), 83.27 (d, C-4''), 69.33 (C-5''), 18.55 (q, C-6''), 58.81 (q, C-7''), 106.20 (d, C-1'''), 75.08 (d, C-2'''), 87.82 (d, C-3'''), 75.87 (d, C-4'''), 72.76 (d, C-5'''), 18.53 (q, C-6'''), 60.98 (q, C-7'''), The structures of (Ⅰ) and (Ⅱ) were given in the following Chart The detail study in progress will be reported in another paper.